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(71)Applicant : KANSAI PAINT CO LTD

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(72)Inventor : ADACHI NAOHITO  
KAWAMOTO TORIMOTO  
HARAKAWA HIROMI

## (54) HEAT CURING-TYPE POWDER COATING COMPOSITION

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide a heat curing-type powder coating composition excellent in acid resistance and a finished outward appearance.

SOLUTION: The heat curing-type powder coating composition features comprising (I) a mixed resin between (A) an epoxy group-containing vinyl-based resin containing 20-70 wt.% of an epoxy group-containing vinyl-based monomer and having a glass transition temperature of 30° C to 100° C and (B) an epoxy group-containing vinyl-based resin containing 20-70 wt.% of an epoxy group-containing vinyl-based monomer and having a glass transition temperature of 30° C to 100° C wherein a solubility parameter of the resin (A) is smaller than that of the resin (B) and a difference between the solubility parameters of resins (A) and (B) is 0.5-1.7 and (II) one or more kinds of acid curing agents as curing resin component selected from the group consisting of a polycarboxylic acid curing agent, a carboxylic anhydride curing agent, and an anhydride curing agent from a polycarboxylic acid and a monocarboxylic acid as curing agents for the above resin basis.

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## CLAIMS

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## [Claim(s)]

[Claim 1] In heat-hardened type powder coatings, the base resinous principle used by these powder coatings The epoxy-group content vinyl system resin within the limits whose glass transition temperature which contains an epoxy-group content vinyl system monomer in this resin 20 % of the weight to 70% of the weight as a radical polymerization nature unsaturation monomer component which constitutes a following (resin I) (A) vinyl system resin is 30 degrees C - 100 degrees C (A), And it is the mixed resin of the epoxy-group content vinyl system resin within the limits of 30 degrees C - 100 degrees C of glass transition temperatures which contain an epoxy-group content vinyl system monomer in this resin 20 % of the weight to 70% of the weight as a radical polymerization nature unsaturation monomer component which constitutes (B) vinyl system resin (B). The soluble parameter of this resin (A) as a curing agent component of the mixed resin whose difference of the soluble parameter of a mutual resin smaller than the soluble parameter of a resin (B) and is within the limits of 0.5-1.7, and the (II) above-mentioned base resin The heat-hardened type powder-coatings constituent characterized by containing one sort or two sorts or more of acid curing agents chosen from a multiple-valued carboxylic-acid curing agent, an anhydrous carboxylic-acid curing agent, and the curing agent of the anhydride of a multiple-valued carboxylic acid and a univalent carboxylic acid as a hardenability resinous principle.

[Claim 2] The heat-hardened type powder-coatings constituent according to claim 1 the thing of 7.9-9.2 within the limits and whose soluble parameter value of an epoxy-group content vinyl system resin (B) the soluble parameter values of an epoxy-group content vinyl system resin (A) are mixed resins with the thing of 9.6-10.9 within the limits for a mixed resinous principle (I).

[Claim 3] The heat-hardened type powder-coatings constituent according to claim 1 or 2 which is 5 % of the weight - 60% of the weight of within the limits as an epoxy-group content vinyl system resin (A) as a radical polymerization nature unsaturation monomer component from which the monomer of styrene and/or isobornyl (meta) acrylate constitutes this resin (A).

[Claim 4] A heat-hardened type powder-coatings constituent given in the claim 1 whose mixed rate of the epoxy-group content vinyl system (resin A) / epoxy-group content vinyl system resin (B) is within the limits of 10 / 90 - 90/10 by the weight ratio in a mixed resinous principle (I), or any 1 term of 3.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[The technical field to which invention belongs] this invention is based on the thermosetting new powder-coatings constituent which can form the paint film excellent in weatherability, solvent resistance, acid resistance, and result appearance, and it is suitable for the fine-particles clear paint painted especially on a base paint.

#### [0002]

[Description of the Prior Art] finishing of a former and automobile shell plate -- the paint film which thermosetting powder coatings are painted as clear and formed there must be finished from the use, and must be filling the demand of appearance, solvent resistance, acid resistance, weatherability, etc.

[0003] However, result appearance was good, the coexistence with the solvent resistance to low polar solvents, such as acid resistance, solvent resistance especially MINARARU spirits, and a xylol, was difficult, and the satisfactory thing was not obtained.

#### [0004]

[Means for Solving the Problem] Result appearance is good, and finds out that the heat-hardened type powder-coatings constituent which may be compatible in acid resistance and solvent resistance can be offered, and this invention person etc. came to complete this invention, when a mixed resin was used and the difference of the resin comrade's soluble parameter value used the thing of 0.5-1.7 as a base resinous principle for heat-hardened type fine particles as a result of inquiring wholeheartedly that the above-mentioned trouble should be canceled.

[0005] In 1 and heat-hardened type powder coatings, namely, the base resinous principle used by these powder coatings this invention The epoxy-group content vinyl system resin within the limits whose glass transition temperature which contains an epoxy-group content vinyl system monomer in this resin 20 % of the weight to 70% of the weight as a radical polymerization nature unsaturation monomer component which constitutes a following (resin I) (A) vinyl system resin is 30 degrees C - 100 degrees C (A), And it is the mixed resin of the epoxy-group content vinyl system resin within the limits of 30 degrees C - 100 degrees C of glass transition temperatures which contain an epoxy-group content vinyl system monomer in this resin 20 % of the weight to 70% of the weight as a radical polymerization nature unsaturation monomer component which constitutes (B) vinyl system resin (B). The soluble parameter of this resin (A) as a curing agent component of the mixed resin whose difference of the soluble parameter of a mutual resin smaller than the soluble parameter of a resin (B) and is within the limits of 0.5-1.7, and the (II) above-mentioned base resin The heat-hardened type powder-coatings constituent characterized by containing one sort or two sorts or more of acid curing agents chosen from a multiple-valued carboxylic-acid curing agent, an anhydrous carboxylic-acid curing agent, and the curing agent of the anhydride of a multiple-valued carboxylic acid and a univalent carboxylic acid as a hardenability resinous principle, The soluble parameter value of an epoxy-group content vinyl system resin (A) The thing of 7.9-9.2 within the limits, [ 2 and a mixed resinous principle (I) ] As the heat-hardened type powder-coatings constituent of a publication, 3, and an epoxy-group content vinyl system resin (A) to the above 1 whose soluble parameter value of an epoxy-group content vinyl system resin (B) is a mixed resin with the thing of 9.6-10.9 within the limits The above 1 which is 5 % of the weight - 60% of the weight of within the limits as a radical polymerization nature unsaturation monomer component from which the monomer of styrene and/or isobornyl (meta) acrylate constitutes this resin (A), or a heat-hardened type powder-coatings constituent given in 2, In 4 and a mixed resinous principle (I), it is involved in the above 1 whose mixed rate of the epoxy-group content vinyl system (resin A) / epoxy-group content vinyl system resin (B) is within the limits of 10 / 90 - 90/10 by the weight ratio, or a heat-hardened type powder-coatings constituent given in any 1 term of 3.

#### [0006]

[Embodiments of the Invention] In this specification, a soluble parameter (SP) is the value calculated as follows.

[0007] A soluble parameter (SP) value is a value which it is measured by voice-sound-symbol titration and calculated according to the formula (Journal of Applied Polymer Science, 12, 2359, 1968) of following KW.SHU and J.M.CORBETT.

[0008]

$$SP = \frac{\sqrt{VH} \delta H + \sqrt{VD} \delta D}{\sqrt{VH} + \sqrt{VD}}$$

((VH shows the volumetric fraction of a hexane among a formula) As for the volumetric fraction of deionized water, and deltaH, SP value of a hexane and deltaD show [ VD ] SP value of deionized water)

In the titration of a voice sound symbol, to the inside which dissolved 0.5g (solid content) of dried acrylic copolymers in acetone 10ml, in addition to n-hexane, titration-value [ in a voice sound symbol ] H (ml) is read, titration-value D (ml) in the voice sound symbol which adds deionized water into an acetone solution similarly is read, these are applied to the following formula, and VH, VD, deltaH, and deltaD are computed. In addition, SP values of each solvent are acetone:9.75, n-hexane:7.24, and deionized water:23.43.

[0009]

$$VH = H / (10 + H)$$

$$VD = D / (10 + D)$$

$$\delta H = 9.75 \times 10 / (10 + H) + 7.24 \times H / (10 + H)$$

$$\delta D = 9.75 \times 10 / (10 + D) + 7.24 \times D / (10 + D)$$

Moreover, in this specification, a glass transition temperature is the value calculated by DSC (\*\*\*\* scanning calorimeter).

[0010] the resinous principle (A) and resin (B) component which are used for this invention are mutual -- the glass transition temperature which contains [ as a radical polymerization nature unsaturation monomer component which is alike and constitutes a vinyl system resin ] an epoxy-group content vinyl system monomer preferably in each resin 25 % of the weight to 60% of the weight 20 % of the weight to 70% of the weight -- 30 degrees C - 100 degrees C -- desirable -- 35 degrees C - 80 degrees C and number average molecular weight 1000-20000 -- it is the resin of 1500-15000 within the limits preferably

[0011] If the amount of epoxy-group content vinyl system monomer components contained in a resinous principle (A) and a resin (B) becomes less than 20% of the weight, respectively, hardenability will become bad, on the other hand, if the amount of epoxy-group content vinyl system monomer components exceeds 70 % of the weight, respectively, it will be finished, and appearance becomes bad.

[0012] If the glass transition temperature of a resinous principle (A) and a resin (B) becomes less than 30 degrees C, respectively, the blocking resistance of powder coatings will become bad, and on the other hand, if a glass transition temperature exceeds 100 degrees C, respectively, the result appearance of a paint film will become bad.

[0013] Since the result appearance of a paint film will fall if particles cause weld, a blocking resistance becomes bad and number average molecular weight exceeds 20000, respectively, the powder coatings from which the endurance of a paint film will fall and will be acquired if the number average molecular weight of a resinous principle (A) and a resin (B) becomes less than 1000, respectively are not desirable.

[0014] As the above-mentioned epoxy-group content vinyl system monomer, glycidyl (meta) acrylate, the glycidyl allyl-compound ether, 3, 4-epoxycyclohexyl (meta) acrylate, beta-methyl glycidyl (meta) acrylate, allyl glycidyl ether, etc. are mentioned, for example. these monomers -- one sort -- or two or more sorts can be used, combining Glycidyl (meta) acrylate and beta-methyl glycidyl (meta) acrylate are especially suitable.

[0015] the resin (A) and resin (B) which are used by this invention -- the difference of the soluble parameter of a mutual resin with the soluble parameter of this resin (A) smaller than the soluble parameter of a resin (B) and -- 0.5-1.7 -- the thing of 0.7-1.5 within the limits is used preferably If the difference of a soluble parameter becomes less than 0.5, the acid resistance of a paint film, solvent resistance, etc. will become bad, on the other hand, if the difference of a soluble parameter exceeds 1.7, the compatibility of a resin will become bad and the result appearance of a paint film will fall.

[0016] Moreover, it is desirable as a resin (A) 7.9-9.2, and that a soluble parameter value uses the thing of the range of 8.1-9.0 especially. The effect excellent in paint film performances, such as acid resistance and solvent resistance (especially xylol-proof nature), is demonstrated by going into the range which the soluble parameter value described above.

[0017] On the other hand, it is desirable as a resin (B) 9.6-10.9, and that a soluble parameter value uses the thing of the

range of 9.8-10.7 especially. The effect excellent in paint film performances, such as acid resistance and solvent resistance (especially xylol-proof nature), is demonstrated by going into the range which the soluble parameter value described above.

[0018] As for the mixed rate of a resin (A) and a resin (B), in a mixed resin (I), 10 / 90 - 90/10 especially 20 / 80 - 80/20 are desirable on the basis of both sum total weight %. Since the solvent resistance of a paint film etc. will fall if the blending ratio of coal of a resin (A) becomes less than 10 % of the weight, and the acid resistance of a paint film etc. will fall if the blending ratio of coal of a resin (B) exceeds 90 % of the weight, the blending ratio of coal of a resin (A), on the other hand, exceeds 90 % of the weight and the blending ratio of coal of a resin (B) becomes less than 10% of the weight, it is not desirable.

[0019] It can adjust by choosing suitably and carrying out the radical copolymerization reaction of the radical polymerization nature unsaturation monomer of the remaining following and remaining others which blended the above-mentioned epoxy-group content vinyl system monomer 20 % of the weight to 70% of the weight as a method of adjusting so that it may go into the range of the soluble parameter value which described above the resin (A) and the resin (B), so that it may go into the range of the above-mentioned soluble parameter value.

[0020] Moreover, as a radical polymerization nature unsaturation monomer of the \*\* used by the resin (A), it is desirable to use styrene and/or isobornyl (meta) acrylate ten to 50% of the weight especially preferably five to 60% of the weight. Since the acid resistance of sufficient paint film will fall if less than 5 % of the weight, and the result appearance of a paint film will fall on the other hand if it exceeds 60 % of the weight, it is not desirable. As other radical polymerization nature unsaturation monomers For example, vinyl aromatic compounds, such as styrene, alpha-methyl styrene, vinyltoluene, and alpha-chloro styrene; Methyl (meta) acrylate, Ethyl (meta) acrylate, n-butyl (meta) acrylate, and i-butyl (meta) acrylate, t-butyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, n-octyl (meta) acrylate, desyl (meta) acrylate, Lauryl (meta) acrylate, stearyl (meta) acrylate, Alkyl ester or annular alkyl ester of carbon numbers 1-24 of acrylic acids, such as cyclohexyl (meta) acrylate, isobornyl (meta) acrylate, and tricyclo deca nil (meta) acrylate, or a methacrylic acid etc. is mentioned.

[0021] The curing agents (II) used by this invention are one sort or two sorts or more of curing agents chosen from a multiple-valued carboxylic-acid curing agent (a), an anhydrous carboxylic-acid curing agent (b), and the curing agent (c) of the anhydride of a multiple-valued carboxylic acid and a univalent carboxylic acid.

[0022] Aliphatic dibasic acid, such as a suberic acid, an azelaic acid, a sebacic acid, undecane 2 acid, dodecanedioic acid, tridecanedioic acid, tetradecane 2 acid, pentadecane 2 acid, and eicosane 2 acid, is as specifically as a multiple-valued carboxylic acid (a) used suitably. Specifically as an anhydrous carboxylic-acid curing agent (b), the acid anhydride of aliphatic dibasic acid, such as a suberic acid, an azelaic acid, a sebacic acid, undecane 2 acid, dodecane diacid, tridecanedioic acid, tetradecane 2 acid, pentadecane 2 acid, and eicosane 2 acid, can use it suitably.

[0023] Specifically as a curing agent (c) of the anhydride of a multiple-valued carboxylic acid and a univalent carboxylic acid, what was obtained by-less hydrating aliphatic dibasic acid, such as a suberic acid, an azelaic acid, a sebacic acid, undecane 2 acid, dodecane diacid, tridecanedioic acid, tetradecane 2 acid, pentadecane 2 acid, and eicosane 2 acid, and monobasic acids, such as a palmitic acid, stearin acid, and an eicosanoic acid, can use it suitably.

[0024] In this invention powder coatings, the compound of others, such as a support inhibitor, a surface-control agent, an antioxidant, an ultraviolet ray absorbent, a UV stabilizer, a blocking inhibitor, a flow regulator, an electrification control agent, a color pigment, a bulking agent, and a hardening accelerator, can be blended if needed in addition to the above-mentioned component.

[0025] This invention powder coatings can be manufactured by the well-known fine-particles manufacture method from the former. As the manufacture method of powder coatings, after carrying out the dryblend of a mixed resin (I) and the curing agent (II) with dry-blending machines, such as a Henschel mixer, melting mixture of this blend object can be carried out with melting kneading machines, such as a biaxial melting kneading machine, and it can manufacture cooling, coarse grinding, pulverizing, and by carrying out screen filtration, for example. Moreover, reduced pressure (it heats if needed) dryness of remaining as it is or the thing replaced by water can be carried out for the organic-solvent solution which dissolves or distributes and becomes an organic solvent about a mixed resin (I) and a curing agent (II) besides having described above, and the organic solvent and water can be removed, and it can solidify, and can manufacture coarse grinding, pulverizing, and by carrying out screen filtration. Furthermore, the organic-solvent solution or aquosity liquid which dissolves or distributes and becomes an organic solvent about a mixed resin (I) and a curing agent (II) besides having described above can be freeze-dried, and it can solidify, and can manufacture coarse grinding, pulverizing, and by carrying out screen filtration.

[0026] This invention powder coatings like the conventional powder coatings For example, steel, aluminum, On material front faces, such as a paint processing material which gave the primer, middle-coat paint, and under coat base paint of the surface treatment material which performed surface treatment, such as phosphoric acid zinc, to metal

materials, such as zinc, tin, copper, and melting galvanization, and this metal material, or electropainting. Usually, the thickness after printing carries out powder coating of the about 10-200 micrometers by the methods of application, such as electrostatic spray painting, triboelectrification spray painting, and fluidized bed coating, so that it may become the range of about 20-150 micrometers preferably. subsequently For example, about 120 degrees C - 300 degrees C of hardening paint films can be preferably formed for about 10 - 60 minutes by baking for [ for / about 20 minutes / - ] 40 minutes preferably at the printing temperature of about 140 degrees C - 200 degrees C.

[0027]

[Effect of the Invention] the resin (B) which uses the resin (A) component which uses this invention powder coatings in these paints combining this resin -- a soluble parameter -- a low sake -- a resin (A) component -- the upper layer of a hardening paint film -- and result appearance, such as smooth nature on the front face of a paint film which a fine-particles particle carries out a heat flow, and comes to form a paint film, and gloss, thinks that a good thing is obtained so that a resin (B) component may exist in the lower layer mostly. Moreover, since the formed upper paint film is a low polar paint film, cannot get wet easily to polar high corrosion matter, such as acid rain, and stops being able to permeate further easily into a paint film, it demonstrates the remarkable effect that paint film performances, such as acid resistance, are excellent. Moreover, since a high polarity paint film is formed in a lower layer, as the whole paint film, a low polar solvent, especially the bloating tendency to a xylol are suppressed, and xylol-proof nature demonstrates as a result the remarkable effect of becoming good.

[0028]

[Example] Hereafter, an example is lifted and this invention is explained in detail. In addition, unless it refuses especially, the "section" or "%" expresses weight criteria.

[0029] Having taught the toluene 60 section to the reaction container equipped with the example thermometer of manufacture, the thermostat, the stirrer, the reflux condenser, and dropping equipment of a resin (1), and blowing nitrogen gas into it, it heated at 105 degrees C and the mixed liquor of the styrene 20 section, the methyl methacrylate 10 section, the iso-butyl methacrylate 35 section, the glycidyl methacrylate 35 section, and the azobisisobutyronitril 4 section was dropped over about 3 hours. It was left at 105 degrees C after the dropping end for 1 hour, and further, the azobisisobutyronitril 0.5 section and the toluene 10 section were dropped over 1 hour, it was left at 105 degrees C after the dropping end for 1 hour, and the reaction was ended. Then, reduced pressure operation was performed, the solvent in a system was removed, and the resin (1) was manufactured. The soluble parameters of this resin (A-1) were 9.2, 50 degrees C of glass transition temperatures, and number average molecular weight 5000.

[0030] Having taught the toluene 60 section to the reaction container equipped with the example thermometer of manufacture, the thermostat, the stirrer, the reflux condenser, and dropping equipment of a resin (2), and blowing nitrogen gas into it, it heated at 105 degrees C and the mixed liquor of the styrene 3 section, the methyl methacrylate 57 section, the n-butyl acrylate 5 section, the glycidyl methacrylate 35 section, and the azobisisobutyronitril 4 section was dropped over about 3 hours. It was left at 105 degrees C after the dropping end for 1 hour, and further, the azobisisobutyronitril 0.5 section and the toluene 10 section were dropped over 1 hour, it was left at 105 degrees C after the dropping end for 1 hour, and the reaction was ended. Then, reduced pressure operation was performed, the solvent in a system was removed, and the resin (2) was manufactured. The soluble parameters of this resin (2) were 10.3, 55 degrees C of glass transition temperatures, and number average molecular weight 5000.

[0031] Having taught the toluene 60 section to the reaction container equipped with the example thermometer of manufacture, the thermostat, the stirrer, the reflux condenser, and dropping equipment of a resin (3), and blowing nitrogen gas into it, it heated at 105 degrees C and the mixed liquor of the styrene 20 section, the isobornyl methacrylate 25 section, the iso-butyl methacrylate 20 section, the glycidyl methacrylate 35 section, and the azobisisobutyronitril 4 section was dropped over about 3 hours. It was left at 105 degrees C after the dropping end for 1 hour, and further, the azobisisobutyronitril 0.5 section and the toluene 10 section were dropped over 1 hour, it was left at 105 degrees C after the dropping end for 1 hour, and the reaction was ended. Then, reduced pressure operation was performed, the solvent in a system was removed, and the resin (3) was manufactured. The soluble parameters of this resin (3) were 8.5, 51 degrees C of glass transition temperatures, and number average molecular weight 4800.

[0032] Having taught the toluene 60 section to the reaction container equipped with the example thermometer of manufacture, the thermostat, the stirrer, the reflux condenser, and dropping equipment of a resin (4), and blowing nitrogen gas into it, it heated at 105 degrees C and the mixed liquor of the styrene 15 section, the methyl methacrylate 30 section, the iso-butyl methacrylate 20 section, the glycidyl methacrylate 35 section, and the azobisisobutyronitril 4 section was dropped over about 3 hours. It was left at 105 degrees C after the dropping end for 1 hour, and further, the azobisisobutyronitril 0.5 section and the toluene 10 section were dropped over 1 hour, it was left at 105 degrees C after the dropping end for 1 hour, and the reaction was ended. Then, reduced pressure operation was performed, the solvent in a system was removed, and the resin (4) was manufactured. The soluble parameters of this resin (4) were 9.5, 52

degrees C of glass transition temperatures, and number average molecular weight 5100.

[0033] Having taught the toluene 60 section to the reaction container equipped with the example thermometer of manufacture, the thermostat, the stirrer, the reflux condenser, and dropping equipment of a resin (5), and blowing nitrogen gas into it, it heated at 105 degrees C and the mixed liquor of the styrene 11.5 section, the methyl methacrylate 33.5 section, the n-butyl acrylate 2.5 section, the iso-butyl methacrylate 17.5 section, the glycidyl methacrylate 35 section, and the azobisisobutyronitril 4 section was dropped over about 3 hours. It was left at 105 degrees C after the dropping end for 1 hour, and further, the azobisisobutyronitril 0.5 section and the toluene 10 section were dropped over 1 hour, it was left at 105 degrees C after the dropping end for 1 hour, and the reaction was ended. Then, reduced pressure operation was performed, the solvent in a system was removed, and the resin (5) was manufactured. The soluble parameters of this resin (5) were 9.7, 52 degrees C of glass transition temperatures, and number average molecular weight 5000.

[0034] as a curing agent -- beer nova resin company make -- VXL-1381 (acid anhydride of dodecanedioic acid) was used

[0035] After carrying out the dryblend of the example hard-resin of manufacture (1) 50 section of powder coatings (1), the hard-resin (2) 50 section and the curing agent 40.0 section, and the benzoin 0.5 section by the Henschel mixer at a room temperature, melting kneading was carried out by the extruder. Next, after cooling, it pulverized by the pin disk, it filtered by 150 meshes, and powder coatings (1) were obtained. Powder coatings (2) - (9) was performed like the example of manufacture of powder coatings (1) except changing combination, as shown in a table. A test result is shown in Table 1.

[0036]

[Table 1]  
表1

		実施例1	実施例2	実施例3	比較例1	比較例2	比較例3	比較例4	比較例5	比較例6
混合樹脂(I)	樹脂(A)	1	2	3	4	5	6	7	8	9
	樹脂(B)	A-1	A-1	A-1	A-1	A-2	A-5	A-3	A-4	A-3
	樹脂(B)	A-2	A-2	A-2				A-2	A-2	A-4
	量	樹脂(A)	50	30	70	100	100	50	50	50
		樹脂(B)	50	70	30			50	50	50
硬化剤(II)	VXL-1381	40	40	40	40	40	40	40	40	40
	樹脂(A)	9.2	9.2	9.2	9.2	10.2	9.7	8.5	9.5	8.6
	樹脂(B)	10.3	10.3	10.3	-	-	-	10.8	10.3	9.5
樹脂組成		1.1	1.1	1.1	-	-	-	1.8	0.8	0.9
試験結果	塗膜外観	◎	◎	◎	0	0	◎	x	◎	◎
	耐酸性	0	0	0	0	x	△	0	x	0
	耐キローブ性	0	0	0	x	0	△	0	0	x

[0037] Became 20 microns of dryness thickness about an epoxy system cation electrodeposition paint on a dull steel plate with a thickness of 0.8mm which performed the manufacture (1) coated-object zinc-phosphate chemical conversion of a sample. On the electrodeposited paint film electrodeposited and printed, air-spray paint was carried out so that it might become 25 microns of dryness thickness about an automatic in-the-train coating surfacer, after burning for 30 minutes at 140 degrees C, with the sandpaper of #400, wet sanding was carried out and ridge dryness was carried out, and subsequently it wiped and degreased by petroleum benzine, and considered as the coated object for an examination.

[0038] (2) On the electrodeposited paint film which the epoxy system cation electrodeposition paint was electrodeposited on the dull steel plate with a thickness of 0.8mm which performed the paint film creation condition zinc-phosphate chemical conversion so that it might become 20 microns of dryness thickness, and was printed, after burning an automatic in-the-train coating surfacer so that it may become 20 microns of dryness thickness, wet sanding was carried out with the sandpaper of #400, and ridge dryness was carried out. Subsequently, MAJIKURON base coat HM-22 (the Kansai Paint Co., Ltd. make, a metallic paint, tradename) was painted so that it might become about 15 microns by hardening thickness, printing hardening was carried out for 30 minutes at 140 degrees C with the oven, and it considered as the material for an examination.

[0039] Subsequently, powder coatings were electrostatically painted on the front face of this material so that thickness might become about 50 microns, and they were made it to carry out heat hardening at 160 degrees C with an oven for 30 minutes. The next examination was performed about the obtained color card.

[0040] Paint-film appearance: The following criteria estimated the result appearance of a paint film from a feeling of

gloss, and the smooth feeling. O Although a good thing and O were inferior in smooth nature a little, after heating for 15 minutes on the hot plate which trickled 0.4ml of sulfuric acids into the test color card acid-proof what [ has a good feeling of gloss ], thing [ in which \*\* is inferior a little ], thing [ in which x is inferior ], and :40%, and was heated at 85 degrees C, it rinsed, the painted surface was observed and the following criteria estimated.

O : although it is completely changeless and is normal to the thing \*\*:painted surface, carry out the 0.5mL spot of the xylol on the xylene-proof [ thing ] nature:painted surface few level differences are accepted to be to the boundary of the dropping section and the non-dropped section, and leave it at a room temperature for 30 minutes. Then, after wiping off a xylol by KAZE, visual evaluation of the painted surface is carried out.

O : there is completely nothing with after.

\*\*: A spot section profile can be checked.

x: Swelling clear to the spot section is accepted.

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[Translation done.]

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(71)出願人 000001409

関西ペイント株式会社  
兵庫県尼崎市神崎町33番1号

(72)発明者 安達 尚人

神奈川県平塚市東八幡4丁目17番1号 関  
西ペイント株式会社内

(72)発明者 川本 西元

神奈川県平塚市東八幡4丁目17番1号 関  
西ペイント株式会社内

(72)発明者 原川 浩美

神奈川県平塚市東八幡4丁目17番1号 関  
西ペイント株式会社内

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(54)【発明の名称】 热硬化型粉体塗料組成物

(57)【要約】 (修正有)

【課題】 耐酸性、仕上がり外観に優れた熱硬化型粉体  
塗料組成物を提供する。

【解決手段】 (I) (A)エポキシ基含有ビニル系单  
量体を20重量%~70重量%含有するガラス転移温度  
が30°C~100°Cの範囲内のエポキシ基含有ビニル系  
樹脂(A)、及び(B)エポキシ基含有ビニル系单量体  
を20重量%~70重量%含有するガラス転移温度30  
°C~100°Cの範囲内のエポキシ基含有ビニル系樹脂  
(B)の混合樹脂であって、該樹脂(A)の溶解性パラ  
メーターが樹脂(B)の溶解性パラメーターよりも小さ  
く、且つお互いの樹脂の溶解性パラメーターの差が0.  
5~1.7の範囲内である混合樹脂、及び(I I)上記  
基体樹脂の硬化剤成分として、多価カルボン酸硬化剤、  
無水カルボン酸硬化剤、多価カルボン酸と1価カルボン  
酸の無水物の硬化剤から選ばれる1種もしくは2種以上  
の酸硬化剤を硬化性樹脂成分として含有することを特徴  
とする熱硬化型粉体塗料組成物。

【特許請求の範囲】

【請求項1】 熱硬化型粉体塗料において、該粉体塗料で使用する基体樹脂成分が、下記樹脂(I)(A)ビニル系樹脂を構成するラジカル重合性不飽和单量体成分として該樹脂中にエポキシ基含有ビニル系单量体を20重量%～70重量%含有するガラス転移温度が30℃～100℃の範囲内のエポキシ基含有ビニル系樹脂(A)、及び(B)ビニル系樹脂を構成するラジカル重合性不飽和单量体成分として該樹脂中にエポキシ基含有ビニル系单量体を20重量%～70重量%含有するガラス転移温度30℃～100℃の範囲内のエポキシ基含有ビニル系樹脂(B)の混合樹脂であって、該樹脂(A)の溶解性パラメーターが樹脂(B)の溶解性パラメーターよりも小さく、且つお互いの樹脂の溶解性パラメーターの差が0.5～1.7の範囲内である混合樹脂、及び(II)上記基体樹脂の硬化剤成分として、多価カルボン酸硬化剤、無水カルボン酸硬化剤、多価カルボン酸と1価カルボン酸の無水物の硬化剤から選ばれる1種もしくは2種以上の酸硬化剤を硬化性樹脂成分として含有することを特徴とする熱硬化型粉体塗料組成物。

【請求項2】 混合樹脂成分(I)が、エポキシ基含有ビニル系樹脂(A)の溶解性パラメーター値が7.9～9.2の範囲内のものと、エポキシ基含有ビニル系樹脂(B)の溶解性パラメーター値が9.6～10.9の範囲内のものとの混合樹脂である請求項1に記載の熱硬化型粉体塗料組成物。

【請求項3】 エポキシ基含有ビニル系樹脂(A)として、スチレン及び／又はイソボルニル(メタ)アクリレートの单量体が該樹脂(A)を構成するラジカル重合性不飽和单量体成分として5重量%～60重量%の範囲内である請求項1又は2に記載の熱硬化型粉体塗料組成物。

【請求項4】 混合樹脂成分(I)において、エポキシ基含有ビニル系樹脂(A)／エポキシ基含有ビニル系樹脂(B)の混合割合が重量比率で10/90～90/10の範囲内である請求項1乃至3のいずれか1項に記載の熱硬化型粉体塗料組成物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、耐候性、耐溶剂性、耐酸性、仕上がり外観に優れた塗膜を形成できる新規な熱硬化性粉体塗料組成物によるものであり、特にベース塗料上に塗装される粉体クリヤー塗料に適したものである。

【0002】

【従来の技術及びその課題】 従来、自動車外板の上塗りクリヤーとして熱硬化性粉体塗料が塗装され、そこに形成される塗膜は、その用途から仕上がり外観、耐溶剂性、耐酸性、耐候性等の要求を満たしていかなければならない。

【0003】しかし、仕上がり外観が良好で、耐酸性と耐溶剂性特にミナラスピリッツやキシロール等の低極性溶剤に対する耐溶剂性との両立は難しく、満足なものが得られていなかった。

【0004】

【課題を解決するための手段】 本発明者等は上記した問題点を解消すべく鋭意研究を行った結果、特に熱硬化型粉体用基体樹脂成分として、混合樹脂を使用し、その樹脂同志の溶解性パラメーター値の差が0.5～1.7のものを使用することにより、仕上がり外観が良好で、耐酸性と耐溶剂性を両立しうる熱硬化型粉体塗料組成物を提供できることを見出し、本発明を完成させるに至った。

【0005】即ち、本発明は

1、熱硬化型粉体塗料において、該粉体塗料で使用する基体樹脂成分が、下記樹脂

(I) (A)ビニル系樹脂を構成するラジカル重合性不飽和单量体成分として該樹脂中にエポキシ基含有ビニル系单量体を20重量%～70重量%含有するガラス転移温度が30℃～100℃の範囲内のエポキシ基含有ビニル系樹脂(A)、及び(B)ビニル系樹脂を構成するラジカル重合性不飽和单量体成分として該樹脂中にエポキシ基含有ビニル系单量体を20重量%～70重量%含有するガラス転移温度30℃～100℃の範囲内のエポキシ基含有ビニル系樹脂(B)の混合樹脂であって、該樹脂(A)の溶解性パラメーターが樹脂(B)の溶解性パラメーターよりも小さく、且つお互いの樹脂の溶解性パラメーターの差が0.5～1.7の範囲内である混合樹脂、及び(II)上記基体樹脂の硬化剤成分として、多価カルボン酸硬化剤、無水カルボン酸硬化剤、多価カルボン酸と1価カルボン酸の無水物の硬化剤から選ばれる1種もしくは2種以上の酸硬化剤を硬化性樹脂成分として含有することを特徴とする熱硬化型粉体塗料組成物、

2、混合樹脂成分(I)が、エポキシ基含有ビニル系樹脂(A)の溶解性パラメーター値が7.9～9.2の範囲内のものと、エポキシ基含有ビニル系樹脂(B)の溶解性パラメーター値が9.6～10.9の範囲内のものとの混合樹脂である上記1に記載の熱硬化型粉体塗料組成物、

3、エポキシ基含有ビニル系樹脂(A)として、スチレン及び／又はイソボルニル(メタ)アクリレートの单量体が該樹脂(A)を構成するラジカル重合性不飽和单量体成分として5重量%～60重量%の範囲内である上記1又は2に記載の熱硬化型粉体塗料組成物、

4、混合樹脂成分(I)において、エポキシ基含有ビニル系樹脂(A)／エポキシ基含有ビニル系樹脂(B)の混合割合が重量比率で10/90～90/10の範囲内である上記1乃至3のいずれか1項に記載の熱硬化型粉体塗料組成物に係わる。

【0006】

【発明の実施の形態】 本明細書において、溶解性パラメーター (SP) は次のようにして求めた値である。

【0007】溶解性パラメーター (SP) 値は、濁点滴定によって測定されるものであって、下記K. W. SH

$$SP = \frac{\sqrt{(VH)} \delta H + \sqrt{(VD)} \delta D}{\sqrt{(VH)} \sqrt{(VD)}}$$

(式中、VHはヘキサンの容積分率、VDは脱イオン水の容積分率、 $\delta H$ はヘキサンのSP値、 $\delta D$ は脱イオン水のSP値を示す)

濁点の滴定では、乾燥されたアクリル共重合体(固形分)0.5gをアセトン10mlに溶解した中に、n-ヘキサンに加えてゆき濁点での滴定量H(ml)を読み、同様にアセトン溶液中に脱イオン水を加えての濁点における滴定量D(ml)を読んで、これらを下記式に適用しVH、VD、 $\delta H$ 、 $\delta D$ を算出するものである。

尚、各溶剤のSP値はアセトン:9.75、n-ヘキサン:7.24、脱イオン水:23.43である。

【0009】

$$VH = H / (10 + H)$$

$$VD = D / (10 + D)$$

$$\delta H = 9.75 \times 10 / (10 + H) + 7.24 \times H / (10 + H)$$

$$\delta D = 9.75 \times 10 / (10 + D) + 7.24 \times D / (10 + D)$$

また、本明細書において、ガラス転移温度は、DSC(示差走査熱量計)によって求めた値である。

【0010】本発明に用いられる樹脂成分(A)及び樹脂(B)成分はお互いにビニル系樹脂を構成するラジカル重合性不飽和单量体成分として夫々の樹脂中にエポキシ基含有ビニル系单量体を20重量%~70重量%、好ましくは25重量%~60重量%含有するガラス転移温度が30°C~100°C、好ましくは35°C~80°C、数平均分子量1000~20000、好ましくは1500~15000の範囲内の樹脂である。

【0011】樹脂成分(A)及び樹脂(B)中に含まれるエポキシ基含有ビニル系单量体成分量がそれぞれ20重量%未満になると硬化性が悪くなり、一方、エポキシ基含有ビニル系单量体成分量がそれぞれ70重量%を超えると仕上がり外観が悪くなる。

【0012】樹脂成分(A)及び樹脂(B)のガラス転移温度がそれぞれ30°C未満になると粉体塗料の耐ブロッキング性が悪くなり、一方、ガラス転移温度がそれより100°Cを超えると塗膜の仕上がり外観が悪くなる。

【0013】樹脂成分(A)及び樹脂(B)の数平均分子量がそれぞれ1000未満になると塗膜の耐久性が低下し、また得られる粉体塗料は粒子同士が融着をおこし耐ブロッキング性が悪くなり、数平均分子量がそれぞれ20000を超えると塗膜の仕上がり外観が低下するので好ましくない。

U. J. M. CORBETTの式 (Journal of Applied Polymer Science, 12, 2359, 1968) に準じて計算した値である。

【0008】

$$\sqrt{(VH)} \delta H + \sqrt{(VD)} \delta D$$

【0014】上記エポキシ基含有ビニル系单量体としては、例えば、グリシル(メタ)アクリレート、グリシルアリルエーテル、3、4-エポキシシクロヘキシル(メタ)アクリレート、 $\beta$ -メチルグリシル(メタ)アクリレート、アリルグリシルエーテル等が挙げられる。これらのモノマーは1種あるいは2種以上組み合わせて使用できる。特にグリシル(メタ)アクリレート、 $\beta$ -メチルグリシル(メタ)アクリレートが好適である。

【0015】本発明で使用する樹脂(A)及び樹脂(B)は、該樹脂(A)の溶解性パラメーターが樹脂(B)の溶解性パラメーターよりも小さく、且つお互いの樹脂の溶解性パラメーターの差が0.5~1.7、好ましくは0.7~1.5の範囲内のものが使用される。溶解性パラメーターの差が0.5未満になると、塗膜の耐酸性、耐溶剤性等が悪くなり、一方、溶解性パラメーターの差が1.7を上回ると樹脂の相溶性が悪くなり塗膜の仕上がり外観が低下する。

【0016】また、樹脂(A)として、溶解性パラメーター値が7.9~9.2、特に8.1~9.0の範囲のものを使用することが好ましい。溶解性パラメーター値が上記した範囲に入ることにより耐酸性、耐溶剤性(特に耐キローム性)等の塗膜性能に優れた効果を発揮する。

【0017】一方、樹脂(B)として、溶解性パラメーター値が9.6~10.9、特に9.8~10.7の範囲のものを使用することが好ましい。溶解性パラメーター値が上記した範囲に入ることにより耐酸性、耐溶剤性(特に耐キローム性)等の塗膜性能に優れた効果を発揮する。

【0018】混合樹脂(I)において、樹脂(A)と樹脂(B)との混合割合は両者の合計重量%を基準として10/90~90/10、特に20/80~80/20が好ましい。樹脂(A)の配合割合が10重量%未満となり、そして樹脂(B)の配合割合が90重量%を越えると塗膜の耐酸性などが低下し、一方、樹脂(A)の配合割合が90重量%を超えると塗膜の耐溶剤性などが低下するので好ましくない。

【0019】樹脂(A)及び樹脂(B)を上記した溶解性パラメーター値の範囲に入るように調整する方法としては、上記エポキシ基含有ビニル系单量体を20重量%~70重量%配合した残りの下記その他のラジカル重合性不飽和单量体を上記溶解性パラメーター値の範囲に入

るよう適宜選択してラジカル共重合反応させることにより調整できる。

【0020】また、樹脂(A)で使用するその他のラジカル重合性不飽和単量体としては、特にスチレン及び/又はイソポルニル(メタ)アクリレートを5~60重量%、好ましくは10~50重量%使用することが好ましい。5重量%を下回ると十分な塗膜の耐酸性が低下し、一方、60重量%を上回ると塗膜の仕上がり外観が低下するので好ましくない。その他のラジカル重合性不飽和単量体としては、例えば、スチレン、 $\alpha$ -メチルスチレン、ビニルトルエン、 $\alpha$ -クロロスチレン等のビニル芳香族化合物；メチル(メタ)アクリレート、エチル(メタ)アクリレート、n-ブチル(メタ)アクリレート、i-ブチル(メタ)アクリレート、t-ブチル(メタ)アクリレート、2-エチルヘキシル(メタ)アクリレート、n-オクチル(メタ)アクリレート、デシル(メタ)アクリレート、ラウリル(メタ)アクリレート、ステアリル(メタ)アクリレート、シクロヘキシル(メタ)アクリレート、イソポルニル(メタ)アクリレート、トリシクロデカニル(メタ)アクリレート等のアクリル酸またはメタクリル酸の炭素数1~24のアルキルエステルまたは環状アルキルエステル等が挙げられる。

【0021】本発明で用いられる硬化剤(I I)は、多価カルボン酸硬化剤(a)、無水カルボン酸硬化剤(b)、多価カルボン酸と1価カルボン酸の無水物の硬化剤(c)から選ばれる1種もしくは2種以上の硬化剤である。

【0022】多価カルボン酸(a)としては、具体的には、例えば、スペリン酸、アゼライン酸、セバシン酸、ウンデカン2酸、ドデカン2酸、トリデカン2酸、テトラデカン2酸、ペンタデカン2酸、エイコサン2酸等の脂肪族2塩基酸が好適に用いられる。無水カルボン酸硬化剤(b)としては、具体的には、例えば、スペリン酸、アゼライン酸、セバシン酸、ウンデカン2酸、ドデカン2酸、トリデカン2酸、テトラデカン2酸、ペンタデカン2酸、エイコサン2酸等の脂肪族2塩基酸類の酸無水物が好適に使用できる。

【0023】多価カルボン酸と1価カルボン酸の無水物の硬化剤(c)としては、具体的には、例えば、スペリン酸、アゼライン酸、セバシン酸、ウンデカン2酸、ドデカン2酸、トリデカン2酸、テトラデカン2酸、ペンタデカン2酸、エイコサン2酸等の脂肪族2塩基酸類とパルミチン酸、ステアリン酸、エイコサン酸等の1塩基酸類を無水化することで得られたものが好適に使用することができる。

【0024】本発明粉体塗料において、上記成分以外に必要に応じてワキ防止剤、表面調整剤、酸化防止剤、紫外線吸収剤、紫外線安定剤、ブロッキング防止剤、流動調整剤、帶電抑制剤、着色顔料、充てん剤、硬化促進剤

等のその他の配合物を配合することができる。

【0025】本発明粉体塗料は、従来から公知の粉体製造方法により製造することができる。粉体塗料の製造方法としては、例えば、混合樹脂(I)及び硬化剤(I I)をヘンシェルミキサー等の乾式混合機によりドライブレンドした後、このブレンド物を2軸溶融混練機等の溶融混練機により溶融混合し、冷却、粗粉碎、微粉碎、篩済過することにより製造することができる。また、上記した以外に例えば、混合樹脂(I)及び硬化剤(I I)を有機溶剤に溶解もしくは分散してなる有機溶剤溶液を、そのままもしくは水に置換したものを減圧(必要に応じて加熱)乾燥して有機溶剤や水を除去して固形化し、粗粉碎、微粉碎、篩済過することにより製造することができる。更に、上記した以外に混合樹脂(I)及び硬化剤(I I)を有機溶剤に溶解もしくは分散してなる有機溶剤溶液もしくは水性液を、凍結乾燥して固形化し、粗粉碎、微粉碎、篩済過することにより製造することができる。

【0026】本発明粉体塗料は、従来の粉体塗料と同様に、例えば、鉄鋼、アルミニウム、亜鉛、錫、銅、溶融亜鉛メッキ等の金属素材、該金属素材にりん酸亜鉛等の表面処理を施した表面処理素材又は電着塗装などのプライマーや中塗り塗装や下塗りベース塗装を施した塗装処理素材などの素材表面に、焼付け後の膜厚が通常約10~200 $\mu\text{m}$ 、好ましくは約20~150 $\mu\text{m}$ の範囲になるように、例えば、静電スプレー塗装、摩擦帶電スプレー塗装、流動浸漬塗装等の塗装方法で粉体塗装し、次いで、例えば、約120°C~300°C、好ましくは約140°C~200°Cの焼付け温度で約10~60分間、好ましくは約20分間~40分間焼付けることにより硬化塗膜を形成することができる。

【0027】

【発明の効果】 本発明粉体塗料は、該塗料で使用する樹脂(A)成分は該樹脂と組み合せて使用する樹脂(B)よりも溶解性パラメーターが低いために、樹脂(A)成分は硬化塗膜の上層にそして樹脂(B)成分はその下層に多く存在するように粉体粒子が熱流動して塗膜を形成するようになる塗膜表面の平滑性、光沢等の仕上がり外観が良いものが得られると考える。また、形成された上層塗膜は低極性塗膜であることから、酸性雨等の極性の高い腐食物質に対して濡れ難く、更に塗膜中に浸透し難くなるので耐酸性等の塗膜性能が優れるといった顕著な効果を発揮するものである。また、下層には高極性塗膜が形成されることから、塗膜全体としては低極性の溶剤、特にキシロールへの膨潤性が抑制され、結果として耐キシロール性が良好となるといった顕著な効果を発揮するものである。

【0028】

【実施例】 以下、実施例を掲げて本発明を詳細に説明する。尚、特に断らない限り「部」または「%」は重量

基準を表す。

【0029】樹脂(1)の製造例

温度計、サーモスコット、攪拌器、還流冷却器および滴下装置を備えた反応容器に、トルエン60部を仕込み、窒素ガスを吹き込みながら、105℃に加熱して、スチレン20部、メチルメタクリレート10部、i s o-ブチルメタクリレート35部、グリジルメタクリレート35部、アゾビスイソブチロニトリル4部の混合液を約3時間かけて滴下した。滴下終了後105℃で1時間放置し、更に、アゾビスイソブチロニトリル0.5部、トルエン10部を1時間かけて滴下し、滴下終了後1時間105℃で放置し、反応を終了した。その後、減圧操作を行い、系中の溶剤を除去し、樹脂(1)を製造した。該樹脂(A-1)は溶解性パラメーターが9.2、ガラス転移温度50℃、数平均分子量5000であった。

【0030】樹脂(2)の製造例

温度計、サーモスコット、攪拌器、還流冷却器および滴下装置を備えた反応容器に、トルエン60部を仕込み、窒素ガスを吹き込みながら、105℃に加熱して、スチレン3部、メチルメタクリレート57部、n-ブチルアクリレート5部、グリジルメタクリレート35部、アゾビスイソブチロニトリル4部の混合液を約3時間かけて滴下した。滴下終了後105℃で1時間放置し、更に、アゾビスイソブチロニトリル0.5部、トルエン10部を1時間かけて滴下し、滴下終了後1時間105℃で放置し、反応を終了した。その後、減圧操作を行い、系中の溶剤を除去し、樹脂(2)を製造した。該樹脂(2)は溶解性パラメーターが10.3、ガラス転移温度55℃、数平均分子量5000であった。

【0031】樹脂(3)の製造例

温度計、サーモスコット、攪拌器、還流冷却器および滴下装置を備えた反応容器に、トルエン60部を仕込み、窒素ガスを吹き込みながら、105℃に加熱して、スチレン20部、イソボルニルメタクリレート25部、i s o-ブチルメタクリレート20部、グリジルメタクリレート35部、アゾビスイソブチロニトリル4部の混合液を約3時間かけて滴下した。滴下終了後105℃で1時間放置し、更に、アゾビスイソブチロニトリル0.5部、トルエン10部を1時間かけて滴下し、滴下終了後1時間105℃で放置し、反応を終了した。その後、減圧操作を行い、系中の溶剤を除去し、樹脂(3)を製造した。該樹脂(3)は溶解性パラメーターが8.5、ガラス転移温度51℃、数平均分子量4800であった。

【0032】樹脂(4)の製造例

温度計、サーモスコット、攪拌器、還流冷却器および滴下装置を備えた反応容器に、トルエン60部を仕込み、窒素ガスを吹き込みながら、105℃に加熱して、スチレン15部、メチルメタクリレート30部、i s o-ブチルメタクリレート20部、グリジルメタクリレート35部、アゾビスイソブチロニトリル4部の混合液を約3時間かけて滴下した。滴下終了後105℃で1時間放置し、更に、アゾビスイソブチロニトリル0.5部、トルエン10部を1時間かけて滴下し、滴下終了後1時間105℃で放置し、反応を終了した。その後、減圧操作を行い、系中の溶剤を除去し、樹脂(4)を製造した。該樹脂(4)は溶解性パラメーターが9.5、ガラス転移温度52℃、数平均分子量5100であった。

【0033】樹脂(5)の製造例

温度計、サーモスコット、攪拌器、還流冷却器および滴下装置を備えた反応容器に、トルエン60部を仕込み、窒素ガスを吹き込みながら、105℃に加熱して、スチレン11.5部、メチルメタクリレート33.5部、n-ブチルアクリレート2.5部、i s o-ブチルメタクリレート17.5部、グリジルメタクリレート35部、アゾビスイソブチロニトリル4部の混合液を約3時間かけて滴下した。滴下終了後105℃で1時間放置し、更に、アゾビスイソブチロニトリル0.5部、トルエン10部を1時間かけて滴下し、滴下終了後1時間105℃で放置し、反応を終了した。その後、減圧操作を行い、系中の溶剤を除去し、樹脂(5)を製造した。該樹脂(5)は溶解性パラメーターが9.7、ガラス転移温度52℃、数平均分子量5000であった。

【0034】硬化剤として、ピアノバレジン社製VXL-1381(ドデカン2酸の酸無水物)を使用した。

【0035】粉体塗料(1)の製造例

固体樹脂(1)50部、固体樹脂(2)50部と硬化剤40.0部、ベンゾイン0.5部を室温でヘンシェルミキサーでドライブレンドした後、エクストルーダーで溶融混練した。次に冷却した後、ピンディスクで微粉碎し、150メッシュで済過して粉体塗料(1)を得た。粉体塗料(2)～(9)は配合を表の様に変更する以外は粉体塗料(1)の製造例と同様に行った。試験結果を表1に示す。

【0036】

【表1】

表1

		実測1	実測2	実測3	比較1	比較2	比較3	比較4	比較5	比較6
粉体塗料番号		1	2	3	4	5	6	7	8	9
混合割合(I)	種類 樹脂(A)	A-1	A-1	A-1	A-1	A-2	A-5	A-3	A-4	A-3
	樹脂(B)	A-2	A-2	A-2				A-2	A-2	A-4
量 樹脂(A)	50	30	70	100	100	100	50	50	50	50
	樹脂(B)	50	70	30				50	50	50
耐熱性(II)		VXL-1381	40	40	40	40	40	40	40	40
樹脂 樹脂(A)	樹脂(A)	92	92	92	92	102	97	85	95	86
	樹脂(B)	103	103	103	—	—	—	103	103	95
樹脂差		1.1	1.1	1.1	—	—	—	1.8	0.8	0.9
試験結果		塗膜外観	◎	◎	◎	0	0	◎	◎	◎
耐酸性		0	0	0	0	x	△	0	x	0
耐キシレン性		0	0	0	x	0	△	0	0	x

## 【0037】試料の調製

## (1) 被塗物

磷酸亜鉛化成処理を施した厚さ0.8mmのダル鋼板上にエポキシ系カチオン電着塗料を乾燥膜厚20ミクロンとなるように電着塗装し、焼き付けた電着塗膜上に自動車中塗りサーフェサーを乾燥膜厚25ミクロンとなるようにエアースプレー塗装し、140°Cで30分間焼き付けした後#400のサンドペーパーで水研ぎし、水切り乾燥し、次いで石油ベンジンで拭いて脱脂し試験用被塗物とした。

## 【0038】(2) 塗膜作成条件

磷酸亜鉛化成処理を施した厚さ0.8mmのダル鋼板上にエポキシ系カチオン電着塗料を乾燥膜厚20ミクロンとなるように電着塗装し、焼き付けた電着塗膜上に自動車中塗りサーフェサーを乾燥膜厚20ミクロンとなるように焼き付けした後#400のサンドペーパーで水研ぎし、水切り乾燥した。次いでマジクロンベースコートHM-22(関西ペイント株式会社製、メタリック塗料、商品名)を硬化膜厚で約15ミクロンとなるように塗装し、乾燥器で140°Cで30分間焼付け硬化させ試験用の素材とした。

【0039】次いで該素材の表面に粉体塗料を膜厚が約50ミクロンとなるように静電塗装し、乾燥器で160°Cで30分加熱硬化させた。得られた塗板について次の試験を行った。

【0040】塗膜外観：塗膜の仕上がり外観をツヤ感、平滑感から次の基準で評価した。◎は良好なもの、○は若干平滑性が劣るがツヤ感は良好なもの、△は若干劣るもの、×は劣るもの。

耐酸性：40%硫酸を試験塗板に0.4ml滴下し、85°Cで加熱したホットプレート上で、15分間加熱した後、水洗し、塗面を観察し、次の基準で評価した。

○：全く変化のないもの

△：塗面に異常はないが、滴下部と非滴下部の境界にわずかな段差が認められるもの

耐キシレン性：塗面上にキシロールを0.5mLスポットし、30分室温で放置する。その後、カーゼでキシロールを拭き取った後、塗面を目視評価する。

○：全く剥離がない。

△：スポット部輪郭が確認できる。

×：スポット部に明らかな膨潤が認められる。

## フロントページの続き

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